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'En attendant Debye...'

M Hulin

Equipe de Recherche sur la Diffusion et l'Enseignement de la Physique, Université Pierre et Marie Curie, Tour 32, 4 place Jussieu, 75231 Paris Cedex 05, France

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Abstract The problem of the specific heat of solids and its behaviour at low temperatures played an important role in the evolution of basic ideas in physics at the turn of the century. It was finally solved by Debye, but why did Einstein, who showed a keen interest in that problem for several years, fail to propose the Debye model? This article recalls a few facts and presents a few suggestions.

Résumé Le problème de la chaleur spécifique des solides et de son comportement à basse température a joué un rôle important dans l'évolution des idées fondamentales de la physique au début du siècle. Ce fut Debye qui en apporta la solution, mais on peut se demander pourquoi Einstein, qui manifesta pendant plusieurs années un intérêt soutenu pour ce problème, hésita à proposer ce qui est devenu 'le modèle de Debye'. Cette article rappelle quelques faits et suggère quelques éléments de réponse.

1 Einstein versus Debye: a puzzle within the C_v dilemma

The specific heat of solids was a major problem for physicists at the turn of the century and played an important role in the introduction of quantum ideas. This fact is somewhat obscured in physics teaching by the stress put on atomic physics problems, which generally appear in curricula before solid state physics (e.g. through a discussion of the Bohr model). However, the recollection that one of the earliest recognitions of Albert Einstein as a major 'star' of physics was the invitation extended to him to report on the specific heat of solids at the 1st Solvay Congress of 1911 should suffice to show the importance which was attached to this problem by the leaders of the physics community at that time.

In 1911, Einstein had already made an important contribution to the C_v problem, and the 'Einstein solid' (Einstein 1907) has remained a classical model. It is now emphasised that, while it explained for the first time the low-temperature deviation of C_v from the Dulong–Petit law, this model, with its

unique characteristic frequency ν_E, failed to account quantitatively for the observed behaviour; it predicted a temperature dependence of the specific heat

$$C_v \propto \Phi\left(\frac{h\nu_E}{kT}\right)$$

(where the 'Einstein function' $\Phi(x)$ behaves like $x^2 e^{-x}$ for $x \to \infty$), leading to an exaggerated decrease of C_v when T goes to zero, which does not correspond to the observed T^3 behaviour. It was only with the Debye model (Debye 1912) that the T^3 law was finally understood.

This leaves one with a somewhat puzzling question which we can put in the following way: why did Einstein not propose the 'Debye model'? Einstein was of course quite familiar with the black body problem, and it is nowadays a very conventional remark that a T^3 specific heat means a T^4 internal energy, that is, via Stefan's law, a characteristic of the black body, which it is easy to trace back to the linear dispersion law of electromagnetic waves. A T^3 behaviour of C_v at low temperatures thus seems reasonably direct indication that the solid state thermal properties ought to be explained through the intervention of excitations with, at least at low energies, a linear dispersion law, and acoustic waves (or 'acoustic phonons' if we adopt the modern solid state terminology) appear as the most natural candidates.

With this question in mind, looking through a few original papers[†] of that period firstly gives one some information and secondly raises some questions related to the 'C_v puzzle'; both aspects are considered briefly below.

2 A point of information: the presentation of experimental results

One fact must first be stressed: there was no 'experimental T^3 law' in 1911. Modern textbooks, for the sake of brevity, often present this law at the very beginning of their discussions of the C_v problem, which may leave the impression that the analytical form of the $C_v(T)$ function at low temperatures had already been recognised at the time of Einstein or, a fortiori, Debye. This was not the case.

Actually, the historical development may be summed up in the following way. Deviations from the law of Dulong and Petit, which had been known even at room temperature for some solids (e.g. diamond) since the middle of the 19th century, became more and more frequent when lower temperatures could be reached (that is, when liquid nitrogen, then liquid hydrogen were increasingly used). It was clear that Dulong and Petit had only given a high-temperature asymptotic law. The

[†] The papers by Einstein are described by Lanczos (1974), whose book is a valuable, readily accessible source of great interest.

Einstein model (Einstein 1907) removed the constraint of having C_v fixed at its classical (Dulong and Petit) constant value

$$C_v = 3R;$$

but everybody, including Einstein, admitted from the very beginning that there was no *quantitative* agreement with experimental observations, and that this was to be expected since the unique vibration frequency characterising the Einstein solid was clearly a crude, unrealistic, oversimplification.

However, the impact of the Einstein theory was such that most authors, including experimentalists, were careful not to go too far from it, and made efforts to present their results in the language it had introduced.

A typical example is provided by the experimental 'Nernst–Lindemann formula' (Nernst and Lindemann 1911), which played a major role in the subsequent reflections of Einstein (1911b), Born and von Karman (1912) and Debye (1912). Nernst and Lindemann, at the time the leading experimentalists in the field, showed that their measurements could be accounted for by the sum of two Einstein functions, one with an 'Einstein frequency' one-half of the other. Several remarks are in order.

The Nernst–Lindemann measurements could not be carried out below 20 K, and it would have been very difficult to find a T^3 law. In modern terms, this T^3 behaviour appears for T at most one-tenth or so of the Debye temperature Θ, and if Θ—which is 'a function of T' (actually just a way of saying that the Debye model is not to be taken too seriously on quantitative grounds)—is reasonably constant. This leaves one with quite a restricted domain of variation of T, say between 15 and 35 K or so, where a T^3 law could have been valid, but was very difficult to 'invent' with no *a priori* guess prompted by theoreticians.

In fact, Nernst and his school were content with opening the 'modern' range of temperatures between 100 and 20 K or so; they could not pay too much attention to what was happening at the lower end of this range; and they were very normally satisfied with a clean, and seemingly promising, formulation of their measurements that was closely related to recent theoretical proposals. It remained to theoreticians, as Einstein puts it, to find out why the solid state oscillators spend half their time vibrating at half their normal frequency.

All this provides a nice example of the complex interaction which so frequently occurs between theory and experiment, and a deeper look into the history of that part of solid state physics would not be without interest.

We have not yet tackled what is probably the most puzzling point: the fact that Einstein did not consider acoustic vibrations, which should have appeared as rather natural protagonists in this C_v dilemma. We lack here explicit facts; yet, we may put forward some suggestions.

3 Further, more speculative, remarks

Although he did not have the benefit of the very obvious reasons, connected with the T^3 law, which are set out in modern textbooks, to suggest the introduction of acoustic vibrations as the 'oscillators' of his 1907 model, Einstein felt—and, we could say, from the very beginning—that this model had to be improved by taking into account a variety of excitations, with various frequencies. However, his four-years' research in this field is marked by what appears to be a curious reticence. Thus, although he writes down (Einstein 1911b) the 'modern' formula for U and C_v, involving the density of vibration states, g(ω), and what is now the Bose–Einstein distribution function, together with a summation over frequencies, he remains reluctant to take complete advantage of this formula, and makes no clear attempt to use effectively a whole spectrum of vibrations.

What may have been the reasons for this attitude? We would like to make the few following proposals.

Firstly, Einstein was still quite close to the original derivation of Planck's black body formula, which introduced a 'resonator' in equilibrium with the electromagnetic field. The fundamental reasons for the success of Planck's theory were not at the time fully understood, and Einstein may have wished to be careful not to venture too far from the original theoretical conditions examined in this theory.

It also seems clear that, like other physicists of that period, such as Nernst, Einstein needed to persuade himself that mechanical (acoustical) lattice vibrations effectively played a role in the optical and thermal properties of solids. In several papers (Einstein 1911a,b) he seeks a connection between the 'Einstein frequency' of his model, and other crystal properties, e.g. infrared absorption, compressibility, etc..., and he is a keen observer of experimental results. This search involves dimensional analysis considerations and the repeated use of a 'local model', where the vibrations of an atom on a cubic lattice, elastically interacting with 26 nearest neighbours, are studied. He remarks (Einstein 1911b) that, within the 26-neighbours local model, taking into account these neighbours' own vibrations will profoundly modify the vibration spectrum of the central atom. But he does not make the next step, which is to Fourier-analyse the vibrations of the crystal as a whole, and thus introduce the acoustical waves.

Maybe some mathematical uneasiness has played a role, but it is probable that extending Planck's treatment to such an abstract thing as an acoustical wave, instead of a clearly defined, localised, mechanical-like 'resonator' seemed to Einstein too risky a step to take without many previous cautious considerations.

Finally, one cannot escape the feeling that the problem of the electronic contribution to the specific heat, which we have not mentioned up to

now, always remained present in Einstein's mind. By 1907, atoms had ceased for several years to be regarded as indestructible entities, and, in metals at least, electrons were known to wander through the ionic lattice. They seemed not to contribute to C_v, and this was another puzzling problem (only to be solved with the Pauli principle and Sommerfeld's theory). When proposing his model Einstein (1907) insists on the fact that the 'Einstein frequency', for a vibrating mass m, may be expected to increase as $1/m$; thus the 'Einstein temperature' Θ_E for light particles like electrons will be much higher than room temperature, and the electronic contribution to C_v will be reduced by a factor $\approx e^{-\Theta_E/T} \ll 1$ from its classical value. One of the advantages of Einstein's model is thus that it provides a way out of the electronic specific heat dilemma. Einstein seemingly remained very attentive to this point; it was thus very important for him not to abandon the simple mechanical picture of an oscillator with a definite mass, and this may have led him to refrain from the necessary generalisations.

By contrast, Born and von Karman (1912) and Debye (1912) were much bolder. The formula put forward by Einstein one year earlier, which yields $U(T)$ and $C_v(T)$ starting with $g(\omega)$, is used without undue scruples. The Fourier analysis of lattice vibrations is developed along lines that have remained standard in textbooks since that time; it produces a spectrum that Born and von Karman keep in its original form, while Debye simplifies it to obtain finally the conventional 'Debye model', thus making the decisive final step. All these authors make *no* mention of the electronic contribution to the specific heat.

It is worth noting that Debye notices the analogy between the $C_v \propto T^3$ behaviour at low temperatures and Stefan's law for black body radiation. But he fits his theoretical calculations to the 'Nernst–Lindemann' formula, and his major argument is that the fit he gets is much better than with Einstein's model: the relative deviation does not exceed 15% down to $T = \Theta/10$ (while such a deviation already appears for $T = \Theta/2$ in Einstein's treatment).

As compared with Einstein's cautious ponderings, Debye thus rushes towards the solution of the specific heat dilemma, deliberately ignoring the, not yet ripe, problem of the electronic contribution, and accepting without question the legitimacy of the generalisation of Planck's black body treatment that had been tentatively proposed by Einstein himself. Is it this undue lack of regard to a fundamental problem that motivated the extremely harsh welcome Nernst gave to Debye's theory (Casimir 1977)? Whatever the answer, it is clear that the specific heat question remained, until its end, a fine example of the complexity of scientific progress, and would seem to merit closer historical and epistemological studies.

A final remark: the C_v problem ceased to be a major component of physicists' speculations as soon as Debye had produced his model. (For 15 years or so, solid state physics will almost disappear from the field of pre-quantum physics, and atomic physics will strut in the foreground of the stage. This should not lead us, however, to let our students ignore the important part previously played by solid state considerations.) Perhaps we might also recall that some features of the Debye theory have remained not entirely clear even up to now (Wannier 1966): the extent of its success was partly fortuitous, and it could be worthwhile to try and understand what helped luck in this affair.

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